JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 10, No. 1, January 2008, p. 197 - 200

Freeze-drying synthesis and optical properties of nanocrystalline ZnO/SnO_2 composites

HUAMING YANG *, SHA NIE
Department of Inorganic Materials, School of Resources Processing and Bioengineering, Central South University, Changsha 410083, China

Freeze-drying is a convenient cryochemical powder processing method. In this paper, a novel freeze-drying process was employed to prepare nanosized ZnO/SnO_2 composites with different Zn/Sn molar ratio. X-ray diffraction (XRD) and transmission electronic microscopy (TEM) were used to characterize structure and morphology of the samples. Phases of the Z2S1 (Zn/Sn=2) sample calcined at 700°C are ZnO and SnO_2, while Z1S1 (Zn/Sn=1) and Z1S2 (Zn/Sn=0.5) samples showed peak characteristic of Zn_2SnO_4, which means that excessive SnO_2 is favorable for the formation of Zn_2SnO_4. The band gap observed by ultraviolet-visible (UV-vis) spectroscopy showed that ZnO/SnO_2 composites can be excited by the photons with the wavelength under 418 nm and produces the electron/hole pairs. The ZnO/SnO_2 composites indicated enhanced room-temperature photoluminescence (PL) property with about 4 times of pure ZnO nanoparticles, indicating potential application in optoelectronic devices.

(Received November 26, 2007; accepted January 10, 2008)

Keywords: ZnO/SnO_2 nanocomposites, Freeze-drying synthesis, Microstructure, Optical property

1. Introduction

Improvements in powder processing methods are necessary for preparing submicron and nanostructured powders with a wide range of compositions, sizes and morphologies. Freeze-drying method involves the rapid freezing of a sprayed solution, drying in vacuum by sublimation of the solvent, and decomposition of a salt to oxide by thermal treatment [1]. In comparison with other chemical methods, one of the advantages of freeze-drying method is the ability to synthesize multicomponent polycrystalline powders with controlled characteristics [2]. Furthermore, preparation by freeze-drying method may lead to formation of complex materials with less agglomeration.

Zinc oxide (ZnO) is a material with great potential for a variety of practical applications, such as piezoelectric transducers, chemical and gas sensors, light-emitting diodes and lasers [3]. Its wide bandgap (~3.22 eV at room temperature [4]) makes ZnO a promising photonic material for the UV devices [5]. The synthesis and structural properties of ZnO doped with lithium (Li), cobalt (Co), aluminum (Al) and manganese (Mn) have been reported [6-9]. Some researchers have introduced ZnO/SnO_2 composites [10], most of them paid their attention to its sensitivity [11] or photocatalytic property [12], but little report has been focused on the optical properties of this composites.

In this paper, ZnO/SnO_2 composites were prepared via freeze-drying method, and the influence of Zn/Sn molar ratio on the structure and optical properties of the as-synthesized ZnO/SnO_2 composites were also investigated.

2. Experimental

The synthesis procedures of the ZnO/SnO_2 composites are as follows: $Zn(CH_3COO)_2{\cdot}2H_2O$ and $SnCl_4{\cdot}5H_2O$ in different molar ratios of 2:1 (Z2S1), 1:1 (Z1S1) and 1:2 (Z1S2) were dissolved in a minimum amount of deionized water. Then the 4mol/L of sodium hydroxide (NaOH) solution was added to the above solution to adjust the pH value to about 7.0, and a white precipitate was formed. The resulting precipitate was aged for 24h at ambient temperature, followed by filtering, washing for several times with deionized water and anhydrous alcohol, then dried at -30°C in a Biomedical Freezer (SANYO) for 24h to ice up. The frozen specimen was dehydrated using a freeze-dryer (LGJ-10) operated at -45°C with a pressure of 13-20 Pa to form a precursor. Finally, the precursor was calcined in a furnace (SRJX-4-13) at 700°C for 2h, resulting in the formation of ZnO/SnO_2 composites. Pure ZnO and SnO_2 nanoparticles were prepared in the same procedure as mentioned above except that the starting material was $Zn(CH_3COO)_2{\cdot}2H_2O$ for ZnO and $SnCl_4{\cdot}5H_2O$ for SnO_2, respectively. The pH value of the solution was adjusted to about 10 for ZnO, 2 for SnO_2, respectively.

Crystal structure of the sample was examined by X-ray diffraction (XRD) using a D/max-γ A diffractometer (Cu Kα radiation, λ=0.154056nm) in the diffraction angle

range 2θ=10˚~90˚. Morphology of the sample was observed using JEM-3010 transmission electron microscopy (TEM, Ev=200kV). UV-vis measurements were carried out using a SHIMADZU UV 2450 spectrophotometer. The pure powdered $BaSO_4$ was used as a reference sample. The PL measurements were carried out at room temperature using 254 nm wavelength as the excitation wavelength with a HITACHI FL-4500 type fluorescence spectrometer with a Xe laser as the excitation source.

3. Results and discussion

XRD patterns of the as-synthesized Z2S1 (Zn/Sn=2), Z1S1 (Zn/Sn=1) and Z1S2 (Zn/Sn=0.5) composites calcined at 700°C for 2h are shown in Fig. 1. The phases of the Z2S1 samples calcined at 700°C were ZnO and SnO_2, as for Z1S1 samples, the phases consisted of ZnO, SnO_2 and Zn_2SnO_4, for Z1S2 samples, Zn_2SnO_4 and SnO_2, which means that excessive SnO_2 is favorable for the formation of Zn_2SnO_4. It is in agreement with the literature [13]. Furthmore, the formation temperature of Zn_2SnO_4 is about 700°C, which is about 300°C lower than that (about 1000 °C) with the solid reaction method. [14]

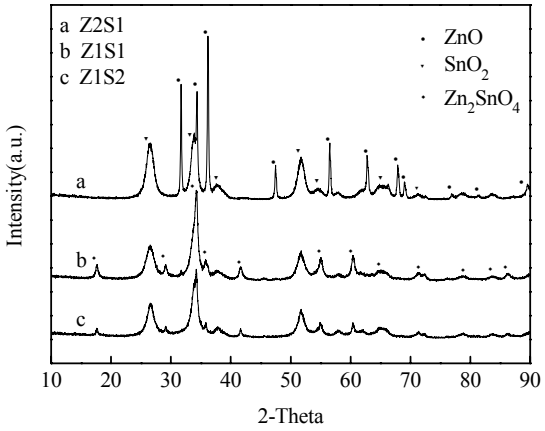

Fig. 1. XRD patterns of as-synthesized Z2S1, Z1S1 and Z1S2 samples calcined at 700°C.

The phase compositions of ZnO/SnO_2 composites calculated according to XRD quantitative analysis from profile-fitting peaks were listed in Table 1. The crystal size of the samples can be calculated according to the Scherrer's formula, the phases and the mean sizes are also listed in Table 1. It is indicating that the crystal size of ZnO decreased with decreasing the Zn/Sn molar ratio. It is reported that the ZnO always has larger grain size than SnO_2 at the same calcination temperature and that the formation of ZnO crystallites was greatly restrained by the presence of SnO_2 [12]. The same results were also obtained here.

Table 1. Crystal size of samples calcined at 700°C.

Sample	Phase	Phase composition (%)	Crystal Size (nm)
Z2S1	ZnO	32.5	34.4
	SnO_2	67.5	10.6
Z1S1	ZnO	7.5	25.9
	SnO_2	62.7	10.3
	Zn_2SnO_4	29.8	15.0
Z1S2	SnO_2	64.8	10.4
	Zn_2SnO_4	35.2	16.6

TEM provides a direct observation of the morphology of materials. The TEM images of calcined Z2S1 composites are shown in Fig. 2. The Z2S1 composites have a spherical morphology with modern aggregation. At the same time, the TEM image also shows that Z2S1 composites are nanometer scale. Compared with co-precipitation method [15], freeze-drying method leads to smaller size of ZnO/SnO_2 composites.

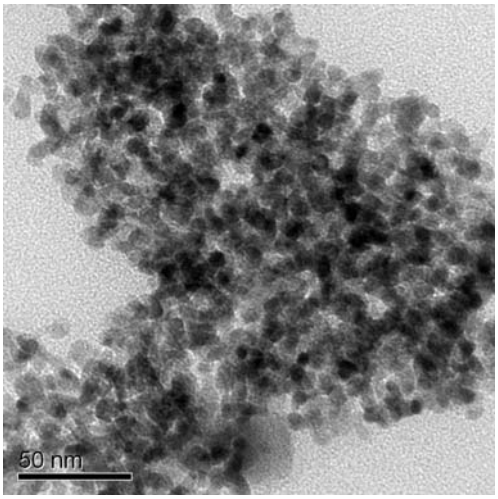

Fig. 2. TEM image of Z2S1 sample.

Fig. 3A shows the UV-vis absorption spectra of ZnO/SnO_2 composites with different Zn/Sn molar ratio. For comparison, the UV-vis absorption spectra of ZnO, Z1S1 and SnO_2 are also presented in Fig. 3B. The wavelengths of absorption edges were determined by extrapolation of the linear part to the x-axis [16]. The absorption edges of Z2S1 and Z1S2 are 402 and 418 nm respectively, corresponding to the band gap energy of 3.08 and 2.97 eV. The absorption edges and the band gap energies are listed in Table 2.

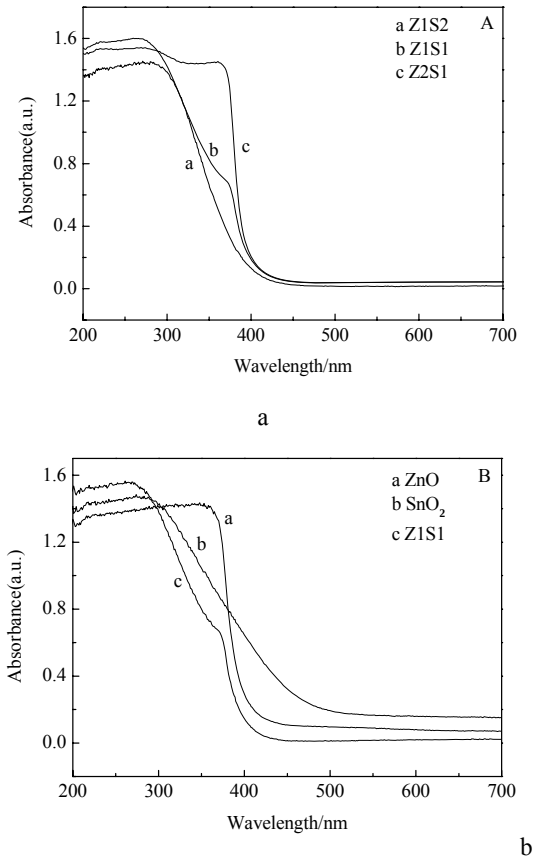

Fig. 3. The UV-vis absorption spectra of products: (a) Zn/Sn molar ratio=0.5,1,2 ; (b) ZnO, Z1S1 and SnO_2

Table 2. Absorption edges and band gap energies of samples.

Sample	Absorption edge (nm)	Band gap energy (eV)
ZnO	399	3.11
Z2S1	402	3.08
Z1S1	412	3.01
Z1S2	418	2.97
SnO_2	500	2.48

The experimental result for the band gap energy of pure ZnO is smaller than that of reported value of 3.22 eV [4]. The band gap energy of pure SnO_2 is 2.48 eV, which is significantly less than the literature of 3.8eV. This phenomenon could probably be attributed to the imperfect crystallization of SnO_2 [13]. Whereas, according to XRD pattern, the SnO_2 sample is of perfect crystallization. Different opinions were reported that SnO_2 is an n-type semiconductor oxide not only with the direct band gap energy of 3.5~3.9 eV but also with the indirect band gap energy of around 2.6 eV [17]. So the experimental result of 2.48 eV should be the indirect band gap energy of SnO_2 in our experiment.

Interestingly, the band gap energy of ZnO/SnO_2 composites decreases with decreasing of Zn/Sn molar ratio. Such shifts may be attributed to the changes of crystallite phase, which seems to be related to the increasing proportion of SnO_2 in composites. The band gap energies of materials are related to the photocatalytic activity of materials for the degradation of pollutants [17]. The band gap observed by UV-vis spectroscopy showed that our ZnO/SnO_2 composites can be excited by the photons with the wavelength under 418 nm and produces the electron/hole pairs, therefore, it may be a promising material in various photocatalytic fields, such as environment purification, decomposition of organic contaminants.

Fig. 4 shows comparative room-temperature PL spectra of ZnO/SnO_2 composites with different Zn/Sn molar ratio. It can be clearly seen that the peak intensity of the ZnO/SnO_2 composite is higher than the pure ZnO nanoparticles. Compared with pure ZnO nanoparticles, the peak intensity of Z1S1 heightens greatly, about 4 times of pure ZnO nanoparticles, which may suggest possible applications in optoelectronic devices. Shalish et al. [16] has reported that below a certain size, the luminescence properties of ZnO nanowires was dominated by properties of the surface, therefore reduction of the crystallite size might cause the relative intensity of visible emission increasing. Fig. 4 also reveals that the peak intensity of the ZnO/SnO_2 composites does not increase with decreasing the Zn/Sn molar ratio, however, reaches a maximal value with the Zn/Sn molar ratio of 1.

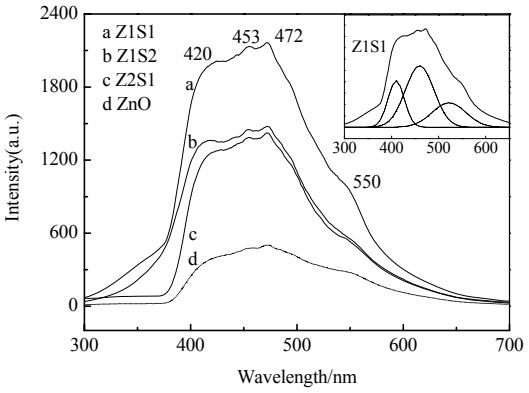

Fig. 4. PL spectra of products excited by 254nm.

Three peaks located at 420nm (2.95eV), 453nm (2.74eV) and 472nm (2.63eV) corresponding to the blue band and another broad peak centered in the green band at around 550nm (2.25 eV) were observed in Fig. 4. It is reported that Sn doping produces red shift of the UV emission, as well as the appearance of strong green

emission in doped ZnO nanowires [17]. Whereas, neither of the four peaks in our samples did exhibit red or blue shift, indicating that no band gap modification due to the changes of crystallite phase has occurred. Tripathy et al. has investigated the photoluminescence of ZnO rod and SnO_2 nanocomposites and received the similar results [18].

Previous studies reported that blue emission was attributed to oxygen vacancies [19], and green emission is the most commonly observed defect emission in ZnO nanostructures. There are many discrepancies on the origin of green emission, including the ionized oxygen vacancy, zinc interstitials [20], Zn-vacancy, donor acceptor pairs [21], and surface states [16]. In our experiment, the green emission might mainly be attributed to the oxygen vacancies or zinc interstitials [22].

4. Conclusions

Nanosized ZnO/SnO_2 composites have been successfully prepared by the freeze-drying method. Phases of the Z2S1 sample calcined at 700 °C are ZnO and SnO_2, while Z1S1 and Z1S2 samples showed peak characteristic of Zn_2SnO_4, which means that excessive SnO_2 is favorable for the formation of Zn_2SnO_4. Crystal size of the samples calculated according to the Scherrer's formula indicated that ZnO has larger grain size than SnO_2 at the same calcination temperature. The TEM image shows that the Z2S1 composites have a spherical morphology and little aggregation. The band gap energy observed by UV-vis spectroscopy is 3.08 eV for Z2S1 compared with those of 3.01 eV for Z1S1 and 2.97 eV for Z1S2. Interestingly, the band gap energy of ZnO/SnO_2 composites decreases with decreasing of Zn/Sn molar ratio. Since the band-gap energies of materials are related to the photocatalytic activity of materials, ZnO/SnO_2 composites as-synthesized may be a promising material for degradating pollutants. The enhanced excellent RT-PL property of ZnO/SnO_2 composites suggests possible applications in optoelectronic devices.

Acknowledgements

The work was supported by the Program for New Century Excellent Talents in University (NCET-05-0695).

References

[1] Z. V. Marinkovi, O. Miloevi, M. V. Nikoli, M. G. Kakazey, Mater. Sci. Eng. **375/377**, 620 (2004).
[2] N. Nikolic, L. Mancic, Z. Marinkovic, Ann. Chim. Sci. Mat. **5**, 35 (2001).
[3] G. Hu, H. Gong, Appl. Phys. Lett., **89**(251102), 1-3 (2006).
[4] M.-K. Leea, H. -F. Tu, J. Appl. Phys. **101**(126103), 1-3 (2007).
[5] J. Grabowska, K. Nanda, E. Mcglynn,. J. Mater. Sci. **16**, 397 (2005).
[6] Y. J. Zeng, Z. Z. Ye, J.G. Lu, W. Z. Xu, Appl. Phys. Lett. **89**(042106), 1 (2006).
[7] J. Cui, Q. Zeng, J. Appl. Phys. **99**(08M113), 1 (2006).
[8] H. P. He, H. P. Tang, Z. Z. Ye, L. P. Zhu, Appl. Phys. Lett. **90**(023104), 1 (2007).
[9] D. Iusan, B. Sanyal, O. Eriksson, J. Appl. Phys. **101**(09H101), 1 (2007).
[10] T. Ivetic, Z. Vukovic, M. V. Nikolic, Ceram. Int. 2007;doi:10.1016/j.ceramint.2007.01.003
[11] K.-W. Kim, P.-S. Cho, S.-J. Kim, J.-H. Lee, Sens. Actuators B **123**, 318 (2007).
[12] M. Zhang, T. An, X. Hu, C. Wang, Appl. Catal. A **260**, 215 (2004).
[13] C. Wang, J. Zhao, X. Wang, Appl. Catal. B **39**, 269 (2002).
[14] F. Belliard, P. A. Connor, J. T. S. Irvine, Solid State Ionics **135**, 163 (2000).
[15] M. Zhang, G. Sheng, J. Fu, Mater. Lett. **59**, 3641 (2005).
[16] I. Shalish, H. Temkin, V. Narayanamurti, Phys. Rev. B **69**(245401), 1 (2004).
[17] S. Y. Bae, C. W. Na, Ja Hee Kang, J. Phys. Chem. B, **109**, 2526 (2005).
[18] S. K. Tripathy, T. Sahoo, I.-H. Lee, Y. -T. Yu, Mater Lett 2007; doi:10.1016/j.matlet 2007.03.007.
[19] L. Wang, X. Z. Zhang, Appl. Phys. Lett. **86**(024108), 1 (2005).
[20] X. Liu, X. Wu, H. Cao, J. Appl. Phys. **95**, 3141 (2004).
[21] H. J. Egelhaaf, D. Oelkrug, J. Cryst. Growth **161**, 190 (1996).
[22] F. K. Shan, G. X. Liu, W. J. Lee, J. Appl. Phys. **101**(053106), 1 (2007).

*Corresponding author: hmyang9392@hotmail.com, hmyang@mail.csu.edu.cn